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## Electrochemical determination of Cd(II) and Pb(II) in mining effluents using a bismuth-coated carbon fiber microelectrode

Roselyn C. Peña,<sup>a</sup> Lorena Cornejo,<sup>ab</sup> Mauro Bertotti<sup>c</sup> and Christopher M. A. Brett<sup>d</sup>

A new bismuth-coated carbon fiber microelectrode (BiFME) has been developed and used for the determination of Cd(II) and Pb(II) by square wave anodic stripping voltammetry (SWASV). The results indicate that cadmium and lead ions give well-defined SWASV peaks with no interference. Linear calibration curves over the range 50–350 nmol L<sup>-1</sup> for both ions were achieved, with detection limits of 9.2 and 10 nmol L<sup>-1</sup> for cadmium and lead, respectively, after applying a 180 s pre-concentration step. Nafion polymer coated BiFMEs were used for decreasing the adsorption of surfactant contaminants, tested with cetyltrimethylammonium bromide (CTAB), Triton X-100 and sodium dodecyl sulfate (SDS) in SWASV of the metal ions. This strategy allowed determination of these trace metal ions in environmental samples, and was employed to determine successfully the concentration of Cd(II) and Pb(II) in samples of mine effluents.

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### 1. Introduction

Heavy metals are difficult to remove from the environment and, unlike many other pollutants, cannot be chemically or biologically degraded and are ultimately indestructible. Today, many heavy metals constitute a global environmental hazard; analyses of air, water and soil samples indicate that the contamination and accumulation of toxic metals are continuously increasing. Therefore, the determination of heavy metals becomes important.<sup>1</sup> The methods routinely used in environmental studies depend mainly on spectroscopic measurements, which sometimes do not allow the quantification of trace concentrations and involve high-cost instrumentation, maintenance and operation. In order to improve on these weak points, water analysis with microelectrodes has been considered as a candidate for novel analyzing systems.<sup>2–8</sup> Electroanalytical techniques combined with microelectrodes show unique properties, such as reduced ohmic drop, capacitive effects, simultaneous detection of several ions and improved material flux, owing to the radial diffusion, hence, much lower limits of detection are obtained.<sup>9,10</sup> Moreover, the response of

microelectrodes is not greatly affected by solution stirring, which is very convenient for on-site measurements.

Electrochemical methods use the possibility to pre-concentrate the analyte on the electrode surface before anodic oxidation of the accumulated material (stripping methods). Thin metal-film electrodes have become widespread in electrochemical stripping analysis due to their relatively simple fabrication and surface regeneration.<sup>11,12</sup> A decade ago, bismuth film electrodes (BFEs) were introduced and have proved to be a convenient alternative to their mercury.<sup>12–14</sup>

Bismuth films are the most common choice to replace mercury in stripping analysis, mainly because bismuth films have attractive properties that include the simple preparation, high sensitivity, well defined and undistorted stripping signal and, generally, present excellent neighboring peak resolution.<sup>15–17</sup> Bismuth is also a more environmentally friendly metal, with very low toxicity in terms of final disposal of laboratory effluents. Bismuth films have been deposited on different carbon substrates, particularly on glassy carbon,<sup>18–21</sup> carbon fiber,<sup>10,13,22</sup> screen-printed carbon,<sup>23–27</sup> carbon paste,<sup>17,28–30</sup> carbon film<sup>31–33</sup> and graphene,<sup>34–44</sup> showing excellent advantages compared to mercury films.

Most analyses of heavy metals are performed on natural samples, which usually contain some substances in their complex matrices that react or often adsorb on the electrode surface, disturbing or blocking the deposition of the analyte. Nafion, a cation-exchange polymer, was used to protect the electrode surface from obstructing materials, as shown at glassy carbon,<sup>45–49</sup> graphite,<sup>50</sup> multi-walled carbon nanotubes,<sup>51</sup> carbon film,<sup>31,32</sup> graphene<sup>52–54</sup> and screen-printed carbon electrodes.<sup>55,56</sup>

<sup>a</sup>Escuela Universitaria de Ingeniería Mecánica, EUDIM, Universidad de Tarapacá, Arica, Chile. E-mail: castaneda.quimica@gmail.com

<sup>b</sup>Laboratorio de Investigaciones Ambientales de Zonas Áridas, LIMZA, Universidad de Tarapacá, Arica, Chile

<sup>c</sup>Departamento de Química Fundamental, Instituto de Química – Universidade de São Paulo, 05508-900 São Paulo, Brazil

<sup>d</sup>Department of Chemistry, Faculty of Sciences and Technology, University of Coimbra, 3004-535 Coimbra, Portugal

Accordingly, the aim of the present work was the fabrication of microelectrodes for the determination of Cd(II) and Pb(II) by square wave anodic stripping voltammetry (SWASV) and investigation of the influence of surfactants on the voltammetric response. Results from the analysis of mine effluent samples are reported and were compared with results from atomic absorption spectrometry (AAS) measurements.

## 2. Experimental

### 2.1. Reagents and solutions

Bismuth(III) nitrate, lead(II) nitrate and cadmium(II) chloride were obtained from Sigma (Germany). Nafion, 5% solution in alcohol, sodium dodecyl sulfate, cetyltrimethylammonium bromide were obtained from Aldrich, Germany and Triton X-100 (Sigma, Germany) was used as received after appropriate dilution. Sodium acetate and acetic acid (Riedel-de Haën, Germany) and Millipore Milli-Q nanopure water were used to prepare 0.1 mol L<sup>-1</sup> acetate buffer, pH 4.5. Stock solutions of the salts mentioned above were prepared in acetate buffer, diluted as required before measurements, and stored at room temperature.

### 2.2. Instrumentation

A three-electrode cell, containing the carbon fiber microelectrode (CFME) ( $r = 11.6 \pm 0.1 \mu\text{m}$ ) as working electrode, a platinum foil counter electrode and a saturated calomel electrode (SCE) as reference, was used for voltammetric measurements. Square-wave and cyclic voltammetry measurements were performed using a computer-controlled  $\mu$ -Autolab type potentiostat – galvanostat with GPES software (Metrohm-Autolab, Utrecht, Netherlands). The pH measurements were performed with a CRISON 2001 micro pH-meter. Experiments were carried out at room temperature ( $25 \pm 1 \text{ }^\circ\text{C}$ ).

For comparative measurements of Cd(II) and Pb(II) in mine effluent samples, atomic absorption spectrometry (AAS) determinations were performed with a Perkin Elmer 3100 AAS spectrometer (Monza, Italy).

### 2.3. CFME fabrication and characterisation

A carbon fiber rod was connected to a Ni/Cr wire with silver paste (Joint Metal Comércio Ltda, São Paulo, Brazil), inserted into a pipette tip which was then insulated with epoxy resin. The microelectrode was left to dry for about 3 h and its surface was polished with sandpaper and alumina, followed by copious washing with distilled water. The radius of the microelectrode was calculated by measuring the limiting diffusion current in a K<sub>3</sub>Fe(CN)<sub>6</sub> solution of known concentration, using 0.1 mol L<sup>-1</sup> KCl as supporting electrolyte, and was found to be 11.6  $\mu\text{m}$ .

### 2.4. SWASV at bismuth film microelectrodes (BiFME)

A Bi film was electrodeposited *in situ* with other metals from a solution containing: 3  $\mu\text{mol L}^{-1}$  Bi(III), Cd(II) + Pb(II), and 0.1 mol L<sup>-1</sup> acetate buffer pH 4.5 on the carbon fiber microelectrode. The SWASV conditions were: accumulation time 180 s at  $-1.3 \text{ V vs. SCE}$ , equilibration time 15 s and, for the square

wave sweep, pulse amplitude 25 mV, frequency 20 Hz, step potential 5 mV, and potential sweep from  $-0.9$  to  $+0.2 \text{ V vs. SCE}$ .

### 2.5. Nafion coated bismuth film electrode

The cation-exchange polymer Nafion was coated on the CFME by applying 5  $\mu\text{L}$  of a 0.25 wt% Nafion solution in ethanol directly on the top of the carbon fiber microelectrode, using a motorized electronic micropipette (EDP-Plus, Rainin, USA). Afterwards, the microelectrode was dried at room temperature.

Bismuth films were formed by *in situ* deposition, Bi(III) was added to the sample being analysed and was co-deposited with the trace cadmium and/or lead by electrodeposition underneath the Nafion coating.

### 2.6. Mine effluent sample analysis

The mine effluent samples were filtered on the day of collection through Millipore membranes (0.45  $\mu\text{m}$ ) to remove suspended particles.

The concentrations of cadmium(II) and lead(II) in mine effluent samples were determined by the standard addition method in order to minimize the influence of the matrix. SWASV was carried out after diluting the mine effluent samples in the supporting electrolyte. The diluted samples were then analyzed after spiking with appropriate amounts of standard metal ion solutions, in order to construct the standard addition plot.

## 3. Results and discussion

### 3.1. Analytical parameters

It has been previously shown that Bi films electrodeposited *in situ* on carbon fiber microelectrodes have an excellent analytical response to Cd and Pb ions and show better repeatability than

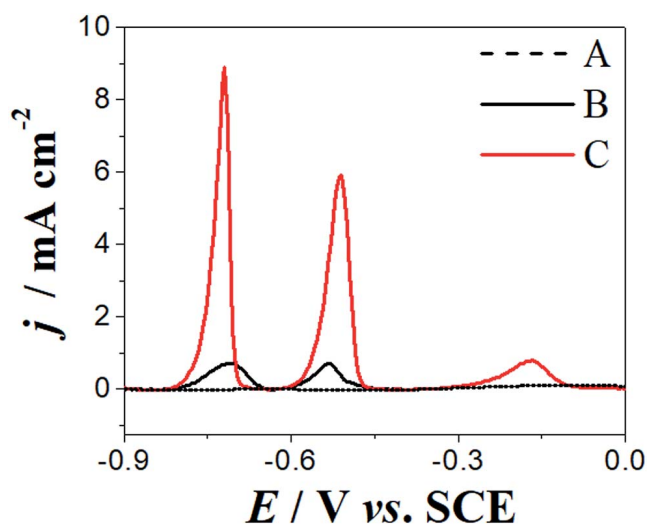


Fig. 1 SWASVs recorded with a carbon fiber microelectrode in 0.1 mol L<sup>-1</sup> acetate buffer pH 4.5 (A) containing 2  $\mu\text{mol L}^{-1}$  Cd(II) and 2  $\mu\text{mol L}^{-1}$  Pb(II) in the absence (B) and presence (C) of 3  $\mu\text{mol L}^{-1}$  Bi(III). Parameters:  $E_{\text{dep}} = -1.3 \text{ V}$ ,  $t_{\text{dep}} = 120 \text{ s}$ ,  $E_{\text{cleaning}} = +0.7 \text{ V}$ ,  $t_{\text{cleaning}} = 60 \text{ s}$ , frequency = 20 Hz,  $E_{\text{step}} = 5 \text{ mV}$ ,  $E_{\text{amplitude}} = 25 \text{ mV}$ .

those prepared *ex situ*.<sup>22</sup> Fig. 1 depicts a typical stripping voltammogram recorded with a CFME carried out in 0.1 mol L<sup>-1</sup> acetate buffer pH 4.5 solution (Fig. 1A) containing 2 μmol L<sup>-1</sup> Cd(II) and 2 μmol L<sup>-1</sup> Pb(II) in the absence (Fig. 1B) and in the presence (Fig. 1C) of 3 μmol L<sup>-1</sup> Bi(III). The signal responses were compared in order to investigate the influence of the bismuth film. The deposition of the bismuth film was made simultaneously with the deposition of Cd(II) and Pb(II) (*in situ* approach). The experimental results showed that Bi(III) has a significant influence on the microelectrode response. Fig. 1B shows the electrode performance without Bi(III): all peaks are well-defined and separated. However, after addition of 3 μmol L<sup>-1</sup> of Bi(III) (Fig. 1C) to the same solution, the peaks increased significantly in height. Stripping peaks remained at the same position for Pb(II) at -0.51 V (Pb oxidation), but there was a small shift to a more negative potential value for Cd, from -0.70 V to -0.72 V (Cd oxidation). Stripping peaks were symmetrical, well-shaped and clearly distinguishable from the background signal, even at very low metal ion concentrations. This can be attributed to the formation of multicomponent alloys. Bismuth is known to form binary or multicomponent alloys with numerous heavy metals (including lead, cadmium, thallium, antimony, indium, or gallium).<sup>12</sup> Recent work has reported that the use of bismuth films contributes to the enhancement of the cadmium and lead signals when the underlying electrode substrate exhibits relatively slow electron transfer properties. However, when the underlying electrode substrate exhibits fast electron transfers kinetics (such as the graphite screen-printed electrodes used throughout), the improvements are not apparent and in some cases can lead to a detrimental effect on the electroanalytical response.<sup>57,58</sup>

Changes in the concentration of Bi(III) have to be considered because a competition can be established during the deposition step. Fig. 2A examines the influence of the Bi(III) concentration upon the resulting stripping response. Both Pb(II) and Cd(II) peaks increased rapidly upon raising the bismuth concentration from 1 to 2 μmol L<sup>-1</sup> for Pb(II) and from 1 to 3 μmol L<sup>-1</sup> for Cd(II). Further increases in the Bi(III) concentration yielded no corresponding increase in the stripping response due to saturation of the small area of the microelectrode. Apparently, a low bismuth coverage is sufficient for depositing the more easily reduced lead ions. A bismuth ion concentration of 3 μmol L<sup>-1</sup> was used in the subsequent analytical experiments.

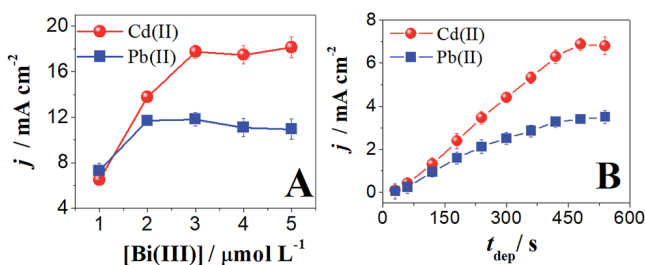


Fig. 2 Effect of Bi(III) concentration (A) and deposition time (B) upon the SWASV response of 2 μmol L<sup>-1</sup> Cd(II) and 2 μmol L<sup>-1</sup> Pb(II) at the *in situ* prepared BiFME. Other conditions are as in Fig. 1.

The dependence of anodic peak current on the pre-concentration time for 2 μmol L<sup>-1</sup> Cd(II) and Pb(II) in 0.1 mol L<sup>-1</sup> acetate buffer (pH 4.5) was also investigated and the results are presented in Fig. 2B. The anodic peak currents increased linearly with increasing pre-concentration time between 60 and 420 s, above which no changes were noticeable. This clear dependence of the stripping current on the deposition time could be used for increasing the sensitivity in SWASV measurements. The deposition time chosen for the determination of Cd(II) and Pb(II) was 180 s, a compromise between increasing the response and the time spent in the analysis. Other optimized parameters were selected considering the best sensitivity, and the values were  $E_{dep} = -1.3$  V,  $E_{cleaning} = +0.7$  V,  $t_{cleaning} = 60$  s, frequency = 20 Hz,  $E_{step} = 5$  mV,  $E_{amplitude} = 25$  mV. Precision was assessed by calculating the relative standard deviation (RSD) of 10 repeated measurements in a solution containing 2 μmol L<sup>-1</sup> Cd(II) and 2 μmol L<sup>-1</sup> Pb(II) in 0.1 mol L<sup>-1</sup> acetate buffer (pH 4.5) (Fig. 3). The values were found to be 5% for Cd(II) and 4% for Pb(II). This excellent repeatability is justified by the absence of stirring during the pre-concentration step, as mass-transport is extremely efficient for microelectrodes.

Under the optimized experimental conditions, calibration plots for Cd(II) and Pb(II) were constructed and a linear relationship for both metal ions was found in the 50 to 350 nmol L<sup>-1</sup> concentration range (Fig. 4A). The equations of the calibration plots were  $I$  (nA) = -0.085 + 0.012 [Cd(II)] (nmol L<sup>-1</sup>) and  $I$  (nA) = 0.012 + 0.006 [Pb(II)] (nmol L<sup>-1</sup>), (Fig. 4B). Other analytical information such as sensitivity and detection limit are presented in Table 1. The detection limit was calculated as the concentration that gives a current response three times the standard deviation of the background signal and the values for Cd(II) and Pb(II) were found to be 9.2 nmol L<sup>-1</sup> and 10 nmol L<sup>-1</sup>, respectively.

The influence of the presence of one metal ion on the anodic peak current corresponding to the other was evaluated in experiments where the concentration of one of the metal ions was varied (20–100 nmol L<sup>-1</sup>) and the other was kept constant (30 nmol L<sup>-1</sup>). The results are shown in Table 2 and it can be observed that lead caused a decrease of 10% in the cadmium signal, when the concentration of Pb(II) was 100 nmol L<sup>-1</sup>. Varying the concentration of cadmium ion, an increase in the lead signal was found. This small difference can be explained by

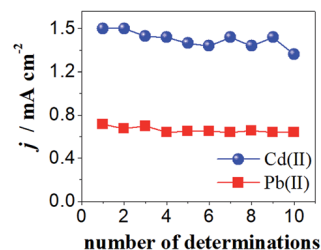


Fig. 3 Repeatability of the measurements obtained with the CFME ( $r = 11.6$  μm) in a solution containing 0.1 mol L<sup>-1</sup> acetate buffer pH ~ 4.5, 2 μmol L<sup>-1</sup> Cd(II), 2 μmol L<sup>-1</sup> Pb(II) and 3 μmol L<sup>-1</sup> Bi(III). Conditions are as in Fig. 1.

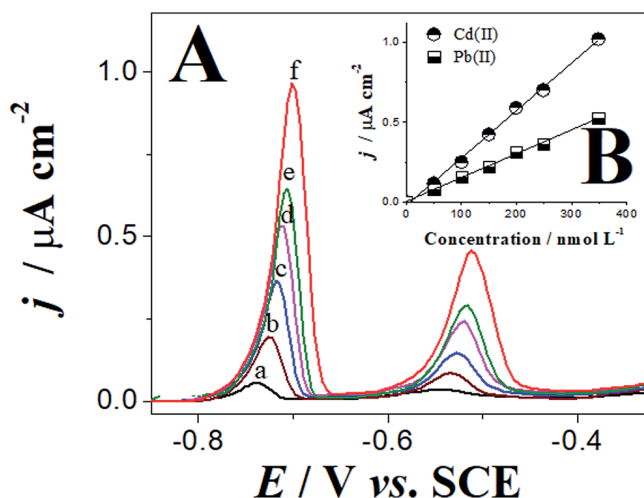


Fig. 4 SWASV in 0.1 mol L<sup>-1</sup> acetate buffer pH ~ 4.5 at BiFME in the presence of 3 μmol L<sup>-1</sup> Bi(III) and different concentrations of Cd(II) and Pb: (a) 50; (b) 100; (c) 150; (d) 200; (e) 250; (f) 350 nmol L<sup>-1</sup> (A). Calibration curves for Cd (circles) and Pb (squares) (B). Parameters:  $E_{\text{dep}} = -1.3$  V,  $t_{\text{dep}} = 180$  s,  $E_{\text{cleaning}} = +0.7$  V,  $t_{\text{cleaning}} = 60$  s, frequency = 20 Hz,  $E_{\text{step}} = 5$  mV,  $E_{\text{amplitude}} = 25$  mV.

Table 1 Parameters of the analytical curves for Cd(II) and Pb(II) obtained with preconcentration time of 180 s using SWASV

Metal	Sensitivity (nA nmol L <sup>-1</sup> cm <sup>2</sup> )	Correlation coefficient ( $R^2$ )	LOD (nmol L <sup>-1</sup> )
Cd	2591	0.9993	9.2
Pb	1308	0.9997	10

Table 2 Effect of the concentration of one metal cation on the recovery of the other cation (30 nmol L<sup>-1</sup>), under the optimized SWASV conditions and accumulation time of 180 s

Metal ion studied	[ ] (nmol L <sup>-1</sup> )	Recovery of Cd(II) (%)	Recovery of Pb(II) (%)
Pb(II)	0	100 ± 2	—
	20	97 ± 4	—
	40	94 ± 3	—
	100	90 ± 5	—
Cd(II)	0	—	100 ± 3
	20	—	105 ± 3
	40	—	105 ± 2
	100	—	106 ± 3

competition of the electrodeposited metals for surface sites and alloy formation, although the interference between metals is not significant.

### 3.2. SWASV detection of Cd(II) and Pb(II) in the presence of surfactants

One of the most common problems in the practical utility of SWASV for trace metal determination is the interference caused by surface-active materials. Surfactants may affect both the deposition and stripping steps during the SWASV

determination due to a slower electron transfer nucleation rates and due to slower diffusion of the analytes to the microelectrode surface.<sup>12</sup> Since environmental samples, in which heavy metals need to be analyzed, usually contain some surface-active substances, it is important to investigate their influence on the analytical performance of bismuth film electrodes. The influence of three surface blocking agents: cetyltrimethylammonium bromide (CTAB), Triton X-100 and sodium dodecyl sulfate (SDS), on the performance of the BiFME was tested.

**3.2.1. BiFME without Nafion.** The influence of the surface-active materials was tested by adding different amounts of these compounds to a known amount of the heavy metal ions for further SWASV analysis. The results are presented in Fig. 5A. Successive additions of CTAB, Triton X-100 and SDS were made in 0.1 mol L<sup>-1</sup> acetate buffer solution (pH 4.5) containing the metal ions and the current signal was monitored. Experiments were repeated in triplicate and gave similar results. Fig. 5A demonstrates that CTAB, Triton X-100 and SDS have different effects on the stripping response. CTAB caused a more severe interference in terms of peak height suppression, compared to Triton X-100 and SDS. An increase in CTAB concentration in the range 0.5–5 mg L<sup>-1</sup> led to a decrease in the peak current for Cd(II) and Pb(II) of 62 and 78%, respectively. High concentrations of CTAB (10–20 mg L<sup>-1</sup>) led to a peak decrease of 88% for both metals.

Low Triton X-100 concentrations of 0.5–5 mg L<sup>-1</sup> did not affect the signal for Cd(II) and Pb(II). A further increase in Triton X-100 concentration (20 mg L<sup>-1</sup>) caused a 46 and 60% signal decrease for Cd(II) and Pb(II), respectively. After successive additions of SDS (0.5–20 mg L<sup>-1</sup>), the metal ions response obtained with the BiFME decreased by 14 and 27% of the initial signal for Cd(II) and Pb(II), respectively.

**3.2.2. Nafion modified BiFME.** Protective films are usually coated onto electrode surfaces to decrease the adsorption of surface active substances.<sup>47</sup> Nafion is a well-known cation-exchange polymer and thus a Nafion layer blocks most anions, while it shows permeability to cations. The Nafion coating is easy to prepare, and the antifouling effect is significant.<sup>59</sup>

Experiments performed with the Nafion-coated BiFME indicated that upon addition of 20 mg L<sup>-1</sup> CTAB (Fig. 5 B), the Cd(II) and Pb(II) response decreases much less in comparison with the response obtained with the BiFME without Nafion coating (a decrease of only 25% for both metals).

After addition of Triton X-100, a decrease in the voltammetric response for Cd(II) and Pb(II) occurred using the Nafion-coated BiFME. However, the influence of this surfactant was less than with the bismuth film electrode without Nafion (40 and 34% for Cd(II) and Pb(II) respectively). Significant changes were observed with the Nafion film for Cd(II) and Pb(II) determination over the concentration range of SDS tested. The metal ion response obtained with the Nafion-coated BiFME decreased by 9.6 and 3.4% of the initial signal for Cd(II) and Pb(II), respectively (Fig. 5B).

The results observed in these experiments can be explained by the properties of the surfactant molecules. CTAB is a cationic

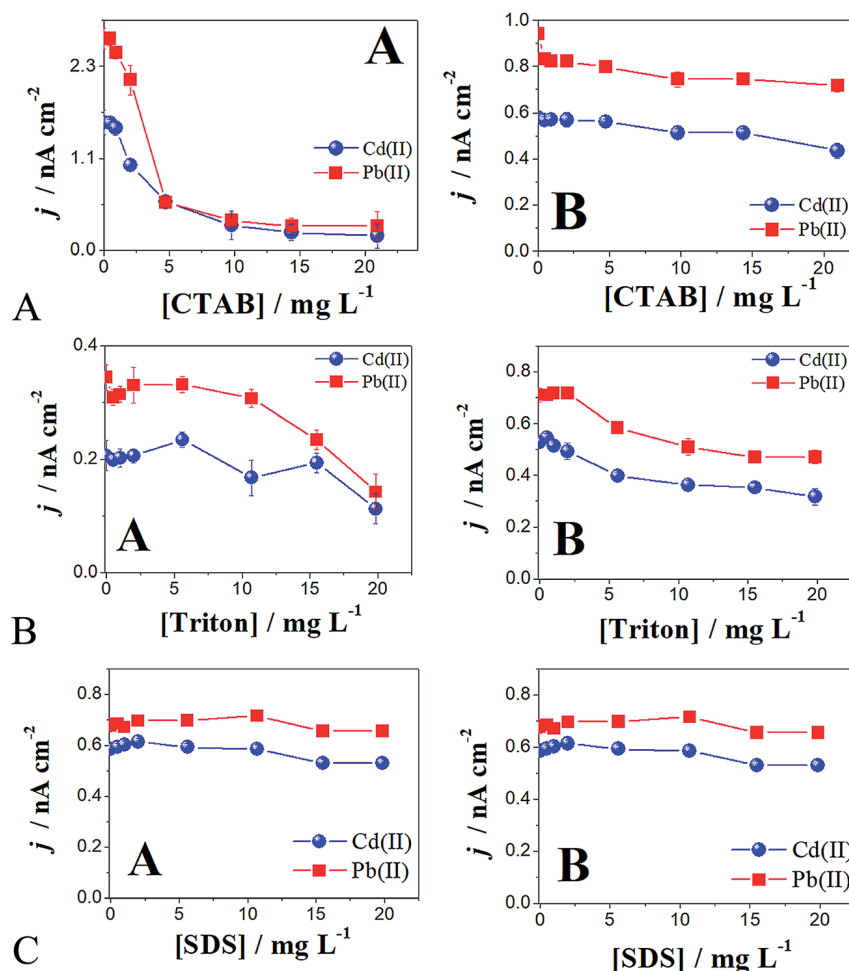


Fig. 5 Influence of different concentrations of: CTAB (A), Triton X-100 (B) and SDS (C) on the SWASV peak heights for a solution containing  $1 \mu\text{mol L}^{-1}$  Cd(II) and  $1 \mu\text{mol L}^{-1}$  Pb(II),  $3 \mu\text{mol L}^{-1}$  Bi(III) in  $0.1 \text{ mol L}^{-1}$  acetate buffer (pH  $\sim 4.5$ ) using a CFME before (A) and after (B) Nafion coating. Conditions are as in Fig. 1.

surfactant and should be attracted to the Nafion membrane; this effect can block the surface of the carbon fiber microelectrode. SDS is an anionic surfactant which is repelled by the Nafion membrane and Triton X-100 is a non-ionic surfactant which adsorbs onto the surface of the microelectrode. Comparing the Nafion-coated BiFME with the BiFME, it is clear that the first is much more tolerant to the presence of surface-active compounds, since the polymeric film forms an effective barrier to the transport of macromolecules to the microelectrode surface. Thus, the Nafion-coated BiFME is a useful tool for the determination of Cd(II) and Pb(II), even in the presence of relatively high concentrations of surfactants.

### 3.3. Application to mine effluent samples

The applicability of the Nafion-coated BiFME to the determination of Cd(II) and Pb(II) in samples of mine effluents was performed. Table 3 shows the Cd(II) and Pb(II) concentrations determined after correction for dilution of the samples, and the results were in good agreement with those obtained by using the AAS method procedure. The paired *t*-test indicated that there was no significant difference between the results

obtained by both methods at a 95% confidence level. As an additional accuracy test of the proposed method, a set of recovery experiments, in which Cd(II) and Pb(II) were added directly to mine effluent samples, was carried out. Recovery results were satisfactory and ranged from 96 to 102%. Accordingly, we can conclude that the proposed method is reliable for Cd(II) and Pb(II) measurements in the investigated samples.

Table 3 Comparison of the results for Cd(II) and Pb(II) content in four samples of mine effluent samples using the proposed SWASV voltammetric procedure and a reference method

Samples	AAS <sup>a</sup> ( $\mu\text{mol L}^{-1}$ )		SWASV ( $\mu\text{mol L}^{-1}$ )	
	Cd(II)	Pb(II)	Cd(II)	Pb(II)
A <sub>1,1</sub>	$7.1 \pm 0.9$	$18.8 \pm 0.6$	$7.9 \pm 0.8$	$18.4 \pm 0.8$
A <sub>1,2</sub>	$1.8 \pm 0.1$	$9.6 \pm 0.3$	$1.8 \pm 0.3$	$9.3 \pm 0.4$
B <sub>2,1</sub>	$3.5 \pm 0.5$	$4.3 \pm 0.4$	$4.1 \pm 0.6$	$4.7 \pm 0.4$
B <sub>2,2</sub>	$5.3 \pm 0.9$	$27.1 \pm 0.5$	$6.2 \pm 0.9$	$26.1 \pm 0.9$

<sup>a</sup> Atomic absorption spectrometry (AAS).

Table 4 Comparison of different sensors for determination of Cd(II) and Pb(II)

Electrode <sup>a</sup>	Technique <sup>b</sup>	$t_{\text{dep}}$ (s)	Linear range (nmol L <sup>-1</sup> )	LOD Cd(II) (nmol L <sup>-1</sup> )	LOD Pb(II) (nmol L <sup>-1</sup> )	Ref.
G/PANI/PS	SWASV	180	48–2400	39.6	15.9	60
NMC	DPASV	150	48–483	13.4	0.24	61
AG-NA/Bi	DPASV	300	24–483	0.62	0.24	52
GC/bixerogel/Nafion	ASV	240	4.8–72	3.0	6.2	62
BiOCl/MWCNT	SWASV	120	24.2–72.5	35.7	9.18	63
Bi/GCE	SWASV	250	24–724	28.5	12.4	64
Bi/Cu/SPE	SWASV	180	1301–13 009	530	830	65
Bi/Sb–Sn/SPE	DPASV	240	24–217	16.1	4.3	66
BiFME	SWASV	180	50–350	9.2	10	This work

<sup>a</sup> G/PANI/PS: graphene/polyaniline/polystyrene, NMC: Nafion-bismuth/nitrogen doped microporous carbon, AG-NA/Bi: bismuth film electrode plated *in situ* using activated graphene, GC/bixerogel/Nafion: bismuth-xerogel/Nafion composite film-modified glassy carbon, BiOCl/MWCNT: multiwalled carbon nanotubes-based composites modified with bismuth-oxychloride, Bi/GCE: glassy carbon electrode modified with bismuth, Bi/Cu/SPE: disposable copper mini-sensor *ex situ* modified bismuth film, Bi/Sb–Sn/SPE: precursor-modified screen-printed sensors. <sup>b</sup> SWASV: square-wave anodic stripping voltammetry, DPASV: differential pulse anodic stripping voltammetry, ASV: Anodic stripping voltammetry.

The analytical performance of the modified BiFME was compared with that of different sensors described in the literature, as shown in Table 4. The linear concentration range extended up to around 350 nmol L<sup>-1</sup> and a deviation from linearity was found at higher Cd(II) and Pb(II) concentrations. Nevertheless, since the experiments were performed with microelectrodes, the precision of the measurements is greatly increased as solution stirring is unnecessary during the pre-concentration step.

## 4. Conclusions

We observed excellent performance analyzing metal ions in aqueous solution by combining square wave anodic stripping voltammetry with a Nafion-coated BiFME. The results show that the Nafion coating decreases the influence of the surfactants on the voltammetric response, especially in the case of CTAB and Triton X-100. Hence, microelectrodes coated with Nafion film and bismuth can be successfully used as sensors for heavy metals in water samples in the presence of surfactants. Concentration values found for Cd(II) and Pb(II) in samples of mine effluents were in good agreement with those obtained by using an independent methodology. The method is reliable, inexpensive and fast and can provide simultaneous information on the concentration of a number of metallic ions.

## Conflicts of interest

There are no conflicts to declare.

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